

Rotational Spectroscopy

Christian Hill

The Diatomic Molecular Hamiltonian

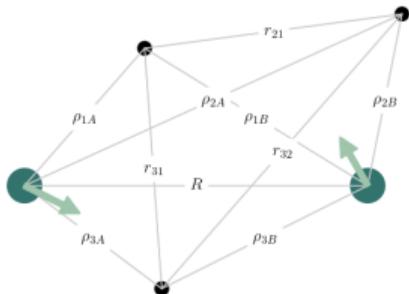
$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\alpha=A,B} \frac{1}{M_\alpha} \nabla_\alpha^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z_A Z_B}{R} + \sum_{i,j < i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z_A}{\rho_{Ai}} + \frac{Z_B}{\rho_{Bi}} \right) \right]$$

The Diatomic Molecular Hamiltonian

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$$-\frac{\hbar^2}{2} \sum_{\alpha=A,B} \frac{1}{M_\alpha} \nabla_\alpha^2$$

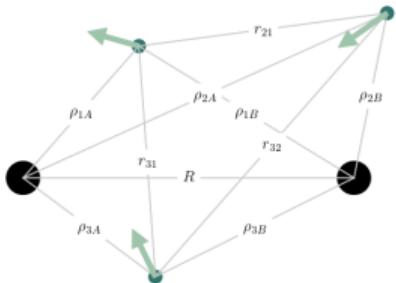
Nuclear kinetic energy



The Diatomic Molecular Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\alpha=A,B} \frac{1}{M_\alpha} \nabla_\alpha^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z_A Z_B}{R} + \sum_{i,j < i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z_A}{\rho_{Ai}} + \frac{Z_B}{\rho_{Bi}} \right) \right]$$

$$-\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 \quad \text{Electronic kinetic energy}$$

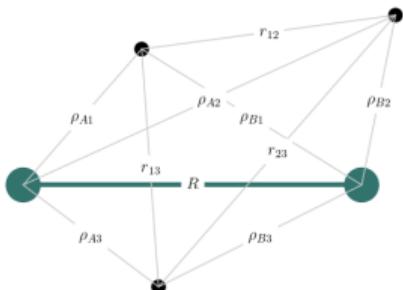


The Diatomic Molecular Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\alpha=A,B} \frac{1}{M_\alpha} \nabla_\alpha^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z_A Z_B}{R} + \sum_{i,j < i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z_A}{\rho_{Ai}} + \frac{Z_B}{\rho_{Bi}} \right) \right]$$

$$\frac{e^2 Z_A Z_B}{4\pi\epsilon_0 R}$$

Nuclear repulsion

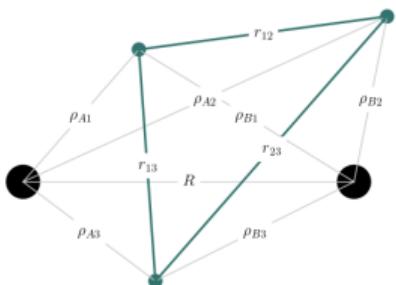


The Diatomic Molecular Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\alpha=A,B} \frac{1}{M_\alpha} \nabla_\alpha^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z_A Z_B}{R} + \sum_{i,j < i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z_A}{\rho_{Ai}} + \frac{Z_B}{\rho_{Bi}} \right) \right]$$

$$\frac{e^2}{4\pi\epsilon_0} \sum_{i,j < i}^N \frac{1}{r_{ij}}$$

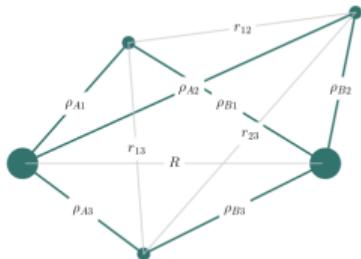
Electron repulsion



The Diatomic Molecular Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\alpha=A,B} \frac{1}{M_\alpha} \nabla_\alpha^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z_A Z_B}{R} + \sum_{i,j < i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z_A}{\rho_{Ai}} + \frac{Z_B}{\rho_{Bi}} \right) \right]$$

$$-\frac{e^2}{4\pi\epsilon_0} \sum_{i=1}^N \left(\frac{Z_A}{\rho_{Ai}} + \frac{Z_B}{\rho_{Bi}} \right) \quad \text{Electron-nuclei attraction}$$



The Diatomic Molecular Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{\alpha=A,B} \frac{1}{M_\alpha} \nabla_\alpha^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z_A Z_B}{R} + \sum_{i,j < i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z_A}{\rho_{Ai}} + \frac{Z_B}{\rho_{Bi}} \right) \right]$$

Coordinate transformation to an origin at the molecular centre of mass, $\mathbf{R}_O: \mathbf{r}'_i = \mathbf{r}_i - \mathbf{R}_O$,
 $\mathbf{R}'_\alpha = \mathbf{R}_\alpha - \mathbf{R}_O$, where:

$$\mathbf{R}_O = \frac{1}{M} \left[m \sum_{i=1}^N \mathbf{r}_i + M_A \mathbf{R}_A + M_B \mathbf{R}_B \right]$$

and $M = Nm + M_A + M_B$ is the total molecular mass. Also eliminate three degrees of freedom by writing $\mathbf{R} = \mathbf{R}_B - \mathbf{R}_A$:

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2M} \nabla_O^2 - \frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla'_i{}^2 - \frac{\hbar^2}{2M} \sum_{i,j=1}^N \nabla'_i \cdot \nabla'_j \\ & + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z_A Z_B}{R} + \sum_{i,j < i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z_A}{\rho_{Ai}} + \frac{Z_B}{\rho_{Bi}} \right) \right] \end{aligned}$$

$\mu = \frac{M_A M_B}{M_A + M_B}$ is the *reduced mass*.

The Diatomic Molecular Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_O^2 - \frac{\hbar^2}{2\mu}\nabla_R^2 - \frac{\hbar^2}{2m_e}\sum_{i=1}^N \nabla_i'^2 - \frac{\hbar^2}{2M}\sum_{i,j=1}^N \nabla_i' \cdot \nabla_j' + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z_A Z_B}{R} + \sum_{i,j < i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z_A}{\rho_{Ai}} + \frac{Z_B}{\rho_{Bi}} \right) \right]$$

$$-\frac{\hbar^2}{2M}\nabla_O^2$$

Translational motion of the molecule as a whole – can be rigorously separated from the internal motion

The Diatomic Molecular Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla'_i{}^2 - \frac{\hbar^2}{2M} \sum_{i,j=1}^N \nabla'_i \cdot \nabla'_j \\ + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z_A Z_B}{R} + \sum_{i,j < i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z_A}{\rho_{Ai}} + \frac{Z_B}{\rho_{Bi}} \right) \right]$$

$$-\frac{\hbar^2}{2M} \sum_{i,j=1}^N \nabla'_i \cdot \nabla'_j$$

Mass-polarization term – small (of the order of effects due to the finite nuclear size) and will be ignored.

The Adiabatic Approximation

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i'^2 + \frac{e^2}{4\pi\epsilon_0} \left[\frac{Z_A Z_B}{R} + \sum_{i,j < i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z_A}{\rho_{Ai}} + \frac{Z_B}{\rho_{Bi}} \right) \right]$$

- The nuclei in a molecule move much more slowly than the electrons: ($m_p/m_e \approx 1836$).
- The electrons adjust their positions rapidly following a change in the internuclear separation.
- The kinetic energy of the nuclear motion ($\hat{T}_{\text{nuc}} = -\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2$) is small compared to that of the electrons.
- Treat \hat{T}_{nuc} as a perturbation to the Hamiltonian for the rigid molecule: $\hat{H} = \hat{H}_0 + \hat{T}_{\text{nuc}}$.

The Adiabatic Approximation

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m_e}\sum_{i=1}^N \nabla_i'^2}_{\hat{T}_{\text{nuc}}} + \underbrace{\frac{e^2}{4\pi\epsilon_0}\left[\frac{Z_A Z_B}{R} + \sum_{i,j < i} \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z_A}{\rho_{Ai}} + \frac{Z_B}{\rho_{Bi}}\right)\right]}_{\hat{H}_0}$$

- Factorize the total molecular wavefunction into the product of a nuclear part and an electronic part: $\psi(\mathbf{r}_i; R) = \chi(\mathbf{R}) \cdot \phi(\mathbf{r}_i; R)$.
- The electronic wavefunction, $\phi(\mathbf{r}_i; R)$, depends *parametrically* on the internuclear separation, R : the effect of the nuclear momenta is ignored.

The Adiabatic Approximation

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2\mu}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2m_e}\sum_{i=1}^N \nabla_i'^2}_{\hat{T}_{\text{nuc}}} + \underbrace{\frac{e^2}{4\pi\epsilon_0}\left[\frac{Z_A Z_B}{R} + \sum_{i,j < i}^N \frac{1}{r_{ij}} - \sum_{i=1}^N \left(\frac{Z_A}{\rho_{Ai}} + \frac{Z_B}{\rho_{Bi}}\right)\right]}_{\hat{H}_0}$$

- The Schrödinger equation, $\hat{H}\psi = E_{n,m}\psi$ is then separable:

$$\begin{aligned}\hat{H}\psi &= \phi \hat{T}_{\text{nuc}} \chi + \chi \hat{H}_0 \phi = E_{n,m} \phi \chi \\ \Rightarrow \frac{1}{\phi} \hat{H}_0 \phi &= -\frac{1}{\chi} \hat{T}_{\text{nuc}} \chi + E_{n,m}\end{aligned}$$

- This equality can only hold if each side is equal to the same constant; (for now) call it $E_n^{(0)}$:

$$\hat{H}_0 \phi = E_n^{(0)} \phi \quad \text{and} \quad \left(\hat{T}_{\text{nuc}} + E_n^{(0)}\right) \chi = E_{n,m} \chi.$$

The Potential Energy Curve

- Solve the electronic Schrödinger equation,

$$\hat{H}_0 \phi(\mathbf{r}_i; R) = E_n^{(0)} \phi(\mathbf{r}_i; R)$$

for different fixed interatomic distances, R .

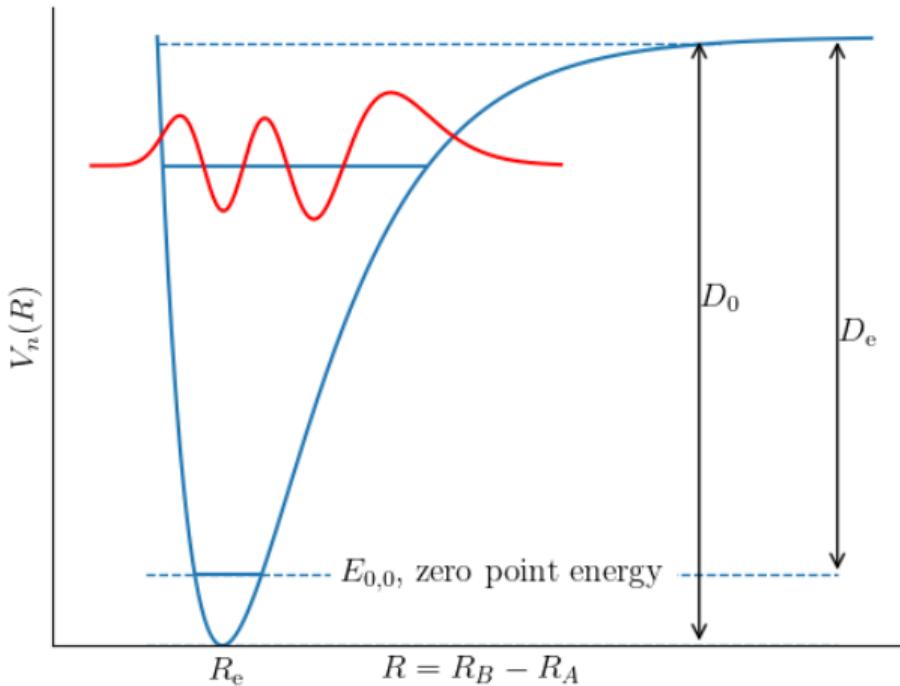
- Then solve for the nuclear motion:

$$\left(\hat{T}_{\text{nuc}} + E_n^{(0)} \right) \chi(\mathbf{R}) = E_{n,m} \chi(\mathbf{R})$$

for the rovibrational states, m , “within” this potential.

- From now on, we will relabel $E_n^{(0)}$ as $V_n(R)$.

The Potential Energy Curve



Separating Rotational and Vibrational Motion

$$\underbrace{\left[-\frac{\hbar^2}{2\mu} \nabla_{\mathbf{R}}^2 + V_n(R) \right]}_{\hat{T}_{\text{nuc}}} \chi(\mathbf{R}) = E_{n,m} \chi(\mathbf{R})$$

- Note that the potential energy does not depend on the angular components of \mathbf{R} : it is spherically symmetric.
- So the nuclear Schrödinger equation is separable, as for the hydrogen atom:

$$\chi(\mathbf{R}) = \chi(R, \theta, \phi) = S(R) \cdot Y(\theta, \phi)$$

Separating Rotational and Vibrational Motion

In spherical polar coordinates,

$$\nabla_{\mathbf{R}}^2 = \underbrace{-\frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right)}_{\nabla_R^2} + \frac{1}{R^2} \left[\underbrace{\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2}}_{\Lambda^2} \right]$$

Using the factored wavefunction, $\chi(\mathbf{R}) = \chi(R, \theta, \phi) = S(R) \cdot Y(\theta, \phi)$, the Schrödinger equation can be rearranged to

$$-\frac{1}{S} R^2 \nabla_R^2 S + \frac{2\mu R^2}{\hbar^2} (V_n(R) - E_{n,m}) = \frac{1}{Y} \Lambda^2 Y.$$

Again, this equality can only hold if both sides are equal to the same constant, C . The angular equation,

$$\Lambda^2 Y = CY,$$

has as its solutions the spherical harmonic functions, $Y(\theta, \phi)$ when $C = -J(J + 1)$ for $J = 0, 1, 2, \dots$

These are the **rotational** wavefunctions.

Separating Rotational and Vibrational Motion

The second equation represents the molecule's **vibrational** motion and rearranges to:

$$\nabla_R^2 S + \frac{2\mu}{\hbar^2} \left[E_{n,m} - V_n(R) - \frac{\hbar^2}{2\mu R^2} J(J+1) \right] S = 0$$

In the case of a **rigid rotor** $R = R_e$ is fixed and $S(R)$ is a constant so $\nabla_R^2 S = 0$. We can choose $V_n(R_e) = 0$ and the energy of the nuclei is therefore

$$E = \frac{\hbar^2}{2\mu R_e^2} J(J+1)$$

The Rigid Rotor

Spectroscopists like to use *term values*,
 $F(J) = E/hc$, in units of cm^{-1} :

$$F(J) = B_e J(J + 1),$$

$$B_e = \frac{\hbar^2}{2hc\mu R_e^2} = \frac{h}{8\pi^2 c I}$$

where $I = \mu R_e^2$ is the *moment of inertia*.

————— $J = 6, E = 42B_e$

————— $J = 5, E = 30B_e$

————— $J = 4, E = 20B_e$

————— $J = 3, E = 12B_e$

————— $J = 2, E = 6B_e$

————— $J = 1, E = 2B_e$

————— $J = 0, E = 0$

Rotational Energy Level Populations

The equilibrium populations of the rotational energy levels are given by statistical mechanics:

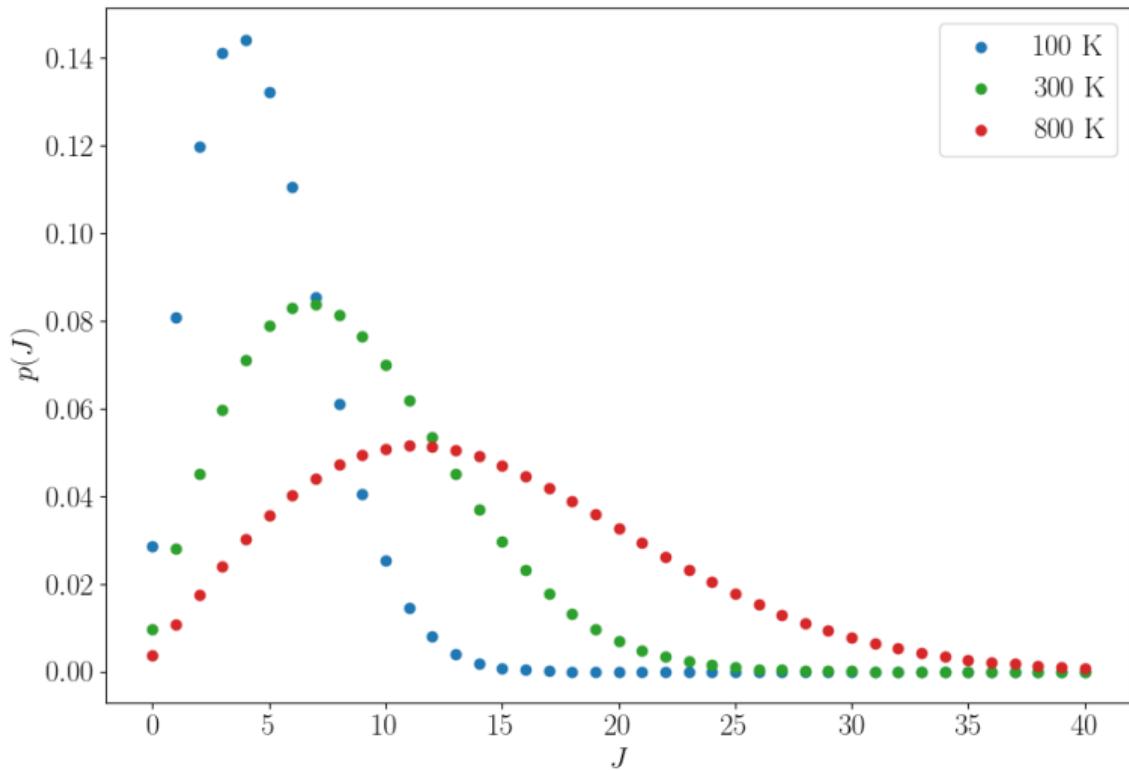
$$p(J) = \frac{g_J \exp\left(-\frac{E_J}{k_B T}\right)}{q(T)},$$

where $g_J = 2J + 1$ is the degeneracy of the J th energy level and

$$q(T) = \sum_{J=0}^{\infty} g_J \exp\left(-\frac{E_J}{k_B T}\right)$$

is the temperature-dependent *partition function*.

Rotational Energy Level Populations



The Rigid Rotor Spectrum

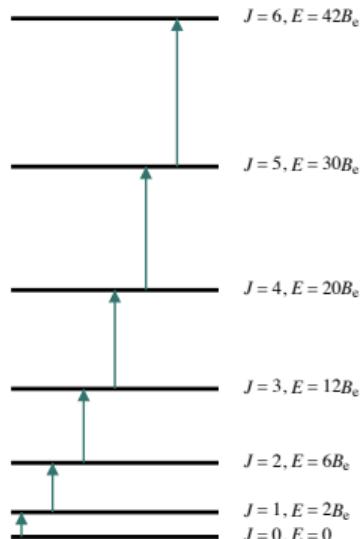
- Electromagnetic radiation can induce a transition between rotational energy levels subject to the selection rule:

$$\Delta J = \pm 1$$

- So absorption and emission occurs at wavenumbers:

$$\tilde{\nu}(J) = F(J+1) - F(J) = 2B_e(J+1).$$

- Lines evenly spaced by $2B_e$.
- Corresponding to:
 - Wavenumbers $0.1 - 100 \text{ cm}^{-1}$
 - Frequency: $10^9 - 10^{12} \text{ Hz}$ (“Gigahertz-Terahertz radiation”)
 - Wavelength: $1 \mu\text{m} - 10 \text{ cm}$ (“microwaves”)



The Rigid Rotor Spectrum

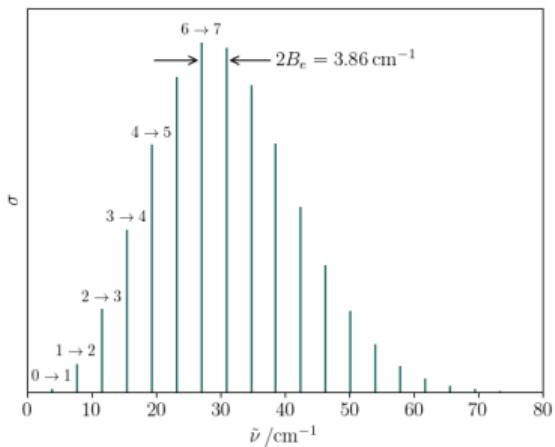
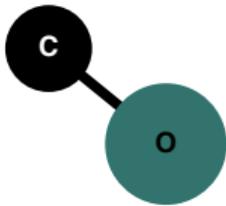
Transition intensities depend on:

- The transition frequency;
- The population difference between the two states involved;
- The permanent electric dipole moment of the molecule, μ_0 ;
- A *Hönl-London factor*: for closed-shell diatomics, this is J or $J + 1$ for $\Delta J = -1$ and $\Delta J = +1$, respectively.

The Rigid Rotor Spectrum

The *net* absorption cross section under equilibrium conditions is:

$$\sigma \propto \mu_0^2 2B_e \frac{(J+1)^2}{q(T)} \exp\left(-\frac{F(J)hc}{k_B T}\right) \left[1 - \exp\left(-\frac{\tilde{\nu}(J)hc}{k_B T}\right)\right]$$



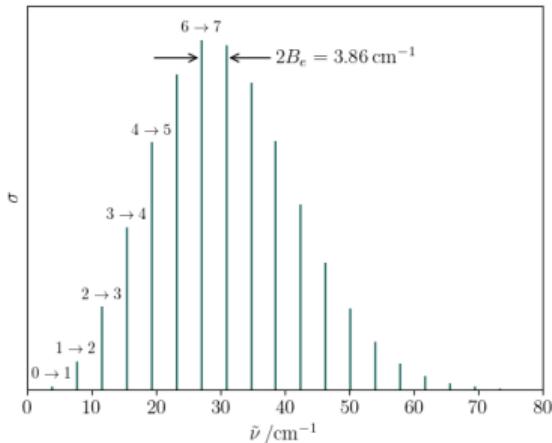
The Rigid Rotor Spectrum

Estimating temperature: the most intense transition in absorption originates on the level¹:

$$J_{\max} = \sqrt{\frac{3k_B T}{2B_e hc}} - \frac{\sqrt{3}}{2} \Rightarrow T \approx \frac{2B_e hc}{k_B} \left(\frac{J_{\max}}{\sqrt{3}} + \frac{1}{2} \right)^2$$

1. R. J. Le Roy, *J. Molec. Spectrosc.* **192**, 237 (1998).

In this case, $J_{\max} = 6$ and
the estimated temperature is
 $T \approx 87$ K.

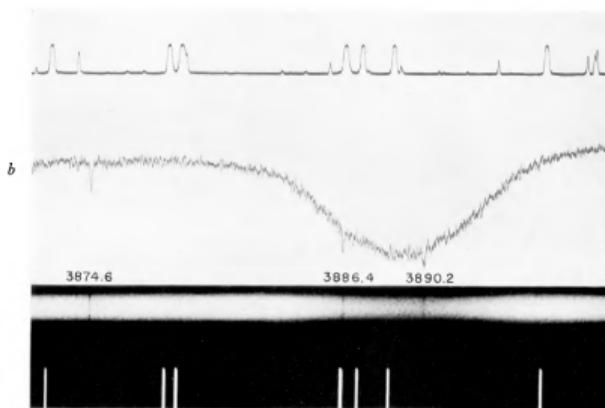


The Rigid Rotor Spectrum

A similar formula applies for the intensities of rotational lines in emission.

Where only two lines can be observed, e.g. in spectra of interstellar space, thermal equilibrium is assumed and the ratio of their intensities used.

e.g. CN spectra of ζ Ophiuchi¹: the lines $J = 0 \rightarrow 1$ at 3874.62 Å and $J = 1 \rightarrow 2$ at 3874.00 Å:



a) α Cygni showing interstellar H and K superposed upon stellar lines; b) ζ Ophiuchi, positive reproduction of stellar and comparison spectra, with photometric tracings. Two lines of CH are shown, $\lambda 3886$ and $\lambda 3890$; also $\lambda 3874.6$ and a trace of $\lambda 3874.8$, both probably CN .

The Rigid Rotor Spectrum

In this case, the intensities are predicted to be in the ratio

$$\frac{I_{1 \rightarrow 2}}{I_{0 \rightarrow 1}} = 2 \exp\left(-\frac{2Bhc}{k_B T}\right)$$

and observed to be in the ratio 5:1, leading to a predicted temperature of 2.3 K¹.

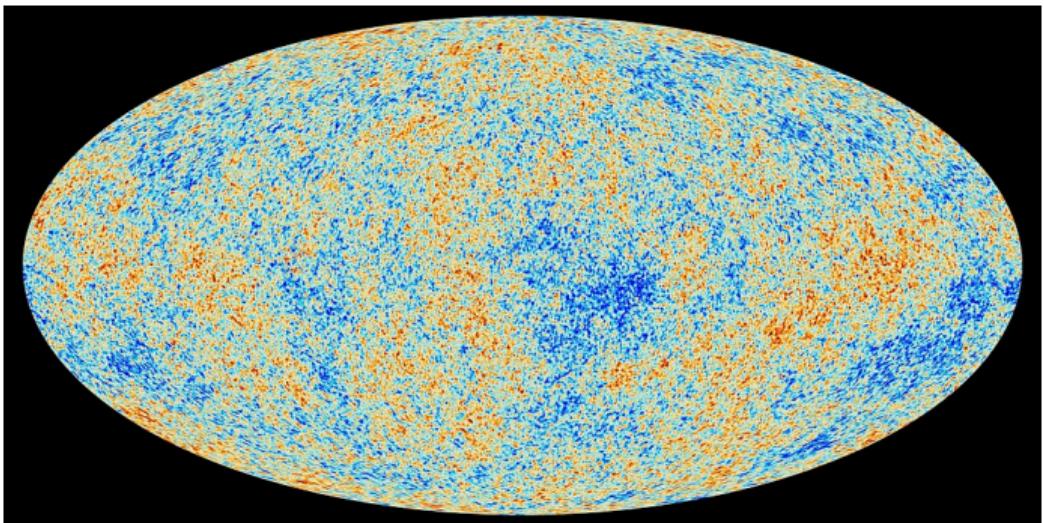
Herzberg wrote²:

[due to the factor ν^4 in (I, 48)]. That is why lines from the second lowest level ($K = 1$) have been observed for CN. From the intensity ratio of the lines with $K = 0$ and $K = 1$ a rotational temperature of 2.3° K follows, which has of course only a very restricted meaning.

1. A. McKellar, *Publications of the Dominion Astrophysical Observatory* 7, 251 (1941).

The Cosmic Microwave Background

Actually closer to 2.7 K.



Temperature map of the cosmic microwave background measured by Planck spacecraft (National Optical-Infrared Astronomy Research Laboratory, licensed under CC BY 4.0)

Centrifugal Distortion

A real molecule is not rigid, but subject to a centrifugal force, $F_c = \mu\omega^2 R$, as it rotates, where the angular velocity, ω , satisfies:

$$E = \frac{1}{2}I\omega^2 = \frac{1}{2}\mu R^2\omega^2 = \frac{\hbar^2}{2\mu R^2}J(J+1)$$

and therefore

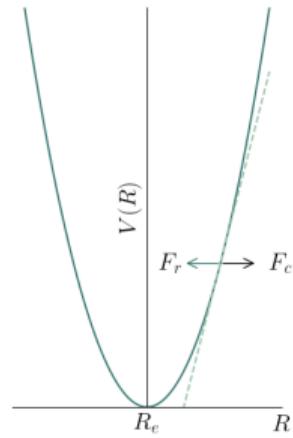
$$F_c = \frac{\hbar^2}{\mu R^3}J(J+1)$$

Centrifugal Distortion

$$F_c = \frac{\hbar^2}{\mu R^3} J(J+1)$$

is balanced
by a restoring force due to the
potential binding the atoms
together:

$$F_r = -\frac{dV_n(R)}{dR}$$



The centrifugal force on a diatomic balanced by
that due to its binding potential

Centrifugal Distortion

- Near the bottom of the potential well $V_n(R)$ may be approximated as a parabola:

$$V_n(R) \approx \frac{1}{2}k(R - R_e)^2$$

- For equilibrium in a given rotational state, J , we must have $F_c = F_r = 0$:

$$\frac{\hbar^2}{\mu R^3} J(J+1) = k(R - R_e)$$

$$\begin{aligned} \Rightarrow R &= R_e + \frac{\hbar^2}{\mu k R^3} J(J+1) \\ &\approx R_e \left(1 + \frac{\hbar^2}{\mu k R_e^4} J(J+1) \right) \end{aligned}$$

Centrifugal Distortion

$R = R_e \left(1 + \frac{\hbar^2}{\mu k R_e^4} J(J+1)\right)$ is to be substituted into

$$E = \frac{\hbar^2}{2\mu R^2} J(J+1)$$

Let $x = \frac{\hbar^2}{\mu k R_e^4} J(J+1) \ll 1$, so we may expand

$$(1+x)^{-2} = (1 - 2x + 3x - \dots)$$

$$R^{-2} = R_e^{-2} \left[1 - \frac{2\hbar^2}{\mu k R_e^4} J(J+1) + \frac{3\hbar^3}{\mu^2 k^2 R_e^8} J^2 (J+1)^2 \dots \right]$$

$$E = \frac{\hbar^2}{2\mu R_e^2} J(J+1) - \frac{\hbar^4}{2\mu^2 k R_e^6} J^2 (J+1)^2 + \frac{3\hbar^6}{2\mu^3 k^2 R_e^{10}} J^3 (J+1)^3$$

Centrifugal Distortion

In terms of wavenumbers:

$$F(J) = B_e J(J+1) - D_e J^2(J+1)^2 + H_e J^3(J+1)^3 + \dots$$

$$B_e = \frac{h}{8\pi^2 \mu c R_e^2}$$

$$D_e = \frac{h^3}{32\pi^4 k \mu c R_e^6}$$

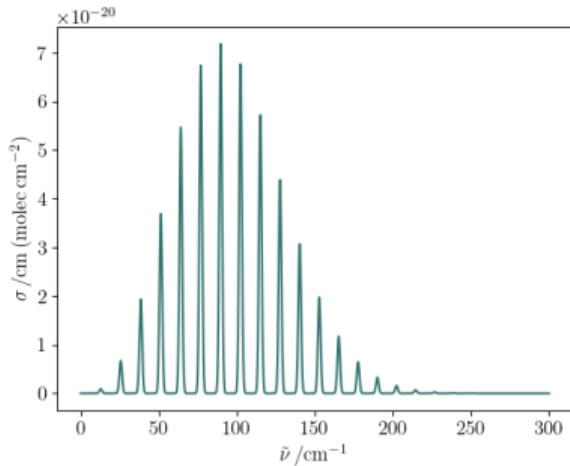
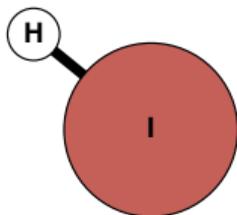
$$H_e = \frac{3h^5}{128\pi^6 k^2 \mu^3 c R_e^{10}}$$

Ignoring higher-order terms,

$$\tilde{\nu}(J) = F(J+1) - F(J) = 2B_e(J+1) - 4D_e(J+1)^3$$

Centrifugal Distortion

Example: the microwave spectrum of hydrogen iodide (HI)

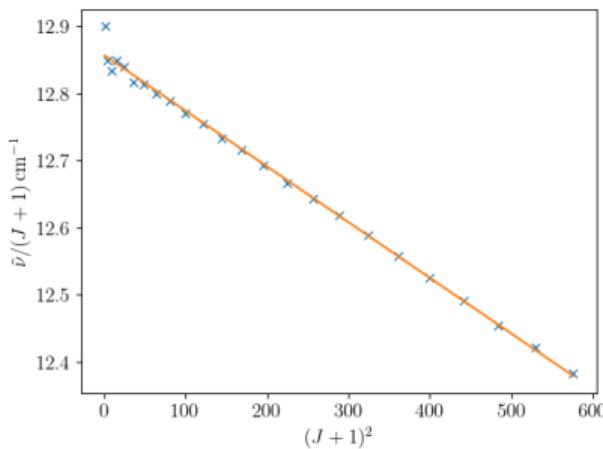


Centrifugal Distortion

Example: the microwave spectrum of hydrogen iodide (HI)

B_e and D_e may be retrieved by linear regression:

$$\frac{\tilde{\nu}(J)}{J+1} = 2B_e - 4D_e(J+1)^2$$



In this case:

$$B_e = 6.42875 \text{ cm}^{-1}$$

$$D_e = 2.077 \times 10^{-4} \text{ cm}^{-1}$$